

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Polyamides

We, INVENTA A.G. FÜR FORSCHUNG UND PATENTVERTWERTUNG, Zürich, a Body Corporate organised under the laws of Switzerland, of Stampfenbachstrasse 38, Zurich 6, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of preparing ternary copolyamides of the type 6/66/12, and to the ternary copolyamides obtained.

There are a large number of known copolyamides of caprolactam and other polyamide-forming monomers, e.g. the copolyamides of caprolactam and hexamethylene diamine adipate (U.S.P. 2 276 437 and U.S.P. 2 320 088), caprolactam and hexamethylene diamine sebacate (U.S.P. 2 359 878) and caprolactam, hexamethylene diamine adipate and hexamethylene diamine sebacate (U.S.P. 2 420 455).

If the batchwise or continuous copolymerisation of the three monomers ϵ -caprolactam, hexamethylene diamine adipate and laurolactam is attempted by the conventional process, that is by hydrolytic polymerisation at 250 to 280°C, difficulties occur during polymerisation, since laurolactam cannot be quantitatively polymerised below 290°C whereas hexamethylene diamine adipate begins to decompose at this temperature. As a result, it is impossible to produce homogeneous ternary copolymers of the required type by the known method.

It has now been discovered that the 6/66/12 copolyamide can be prepared with the components in any desired proportions, and with the monomer units randomly distributed throughout the molecule, and, according to the invention, this is done by heating ϵ -caprolactam or ϵ -aminocaproic acid or both with hexamethylene diamine adipate and poly-

laurolactam in an inert atmosphere at atmospheric pressure to 260—290°C with consequent breakdown of the polylaurolactam to laurolactam monomer units and holding the mixture at this temperature until the random distribution is achieved.

The time required to produce the desired random distribution of monomer units is inversely related to the temperature at which the mixture is held. Polymerisation must be continued for at least 8 hours of the temperature is 290°C, but for at least 12 hours if the temperature is only 260°C. As a general rule, satisfactory polymerisation times are from 8 to 15 hours, and the resultant copolyamides have a low melting point and may be soluble in alcohols depending on the proportions of the monomers. The random nature of the monomer units is demonstrated by this low melting point and solubility in alcohols or alcohol/water or alcohol/benzene mixtures; if the polymerisation is not continued for long enough, the monomer units are not randomly distributed and the copolyamide has properties similar to a block copolyamide.

The mixture to be copolymerised is preferably composed of 10 to 60% by weight of caprolactam or ϵ -aminocaproic acid or both, 10 to 50% by weight of hexamethylene diamine adipate and 5 to 70% by weight of polylaurolactam.

The polylaurolactam should preferably have an average mean degree of polymerisation of 10 to 50, that is a relative viscosity of 1.4 to 1.7 (measured in a 0.5% solution in m-cresol at 20°C). The inert gas can suitably be nitrogen or carbon dioxide.

The molecular weight of the copolyamide product can be regulated in conventional manner by the addition of chain growth regulators of the reactants. Organic carboxylic acids, preferably sebacic acid, can be used for this purpose in the proportion of 1.2—1.5 mol %. Other known chain growth regulators

for caprolactam polymerisation can be used, for example amines, amides, alkali hydroxides and phosphoric acids.

- 5 Copolyamides prepared by the process according to the invention can be used as fusible adhesives, adhesives in solution and adhesives for metal plating. Because of their excellent solubility, they can also be combined with suitable agents such as formalde-
- 10 hyde, epoxy resins and phenol resins to form reactive polyamides which can be cross-linked and therefore useful for textile or paper coatings.

Some Examples will now be given:—

Various proportions of ϵ -aminocaproic acid, 15
hexamethylene diamine adipate and p-lylauro-
lactam having a relative viscosity of 1.6
measured in a 0.5% solution in m.cresol at
20°C were heated with 1.3 mol % of sebacic 20
acid in a nitrogen atmosphere to 270°C and
held at this temperature with stirring for 15
hours. Water liberated by the polymerisation
was removed by the nitrogen bleed.

The proportions of the reactants are given 25
in the following table which also gives the
melting point and solubility of the copolyamide
formed.

Example No.	Reactants (wt %)			6/66/12 copolyamides product	
	Amino-caproic acid %	Hexa-methylene diamine adipate %	Polylauro lactam %	Melting Point °C	Solubility at boiling point in g/100 ml solvent (CH ₃ OH—H ₂ O) 85/15)
1	57	38	5	163—165	>25
2	54	36	10	153—157	>30
3	51	34	15	146—150	>40
4	48	32	20	135—137	>25
5	40	30	30	133—136	>20
6	40	10	50	117—120	3
7	35	15	50	114—116	<4
8	30	40	30	117—120	>15
9	30	30	40	107—110	>10
10	30	25	45	108—111	>10
11	30	20	50	115—119	<2
12	30	15	55	118—120	<2
13	30	10	60	122—124	<1
14	25	30	45	107—109	>15
15	25	25	50	114—116	>10
16	25	15	60	122—125	<1
17	20	40	40	138—140	>15
18	20	30	50	123—125	<1
19	20	20	60	124—127	<1
20	15	25	60	125—130	<1
21	10	40	50	144—147	<2
22	10	30	60	130—133	<3

All the ternary copolyamides in the Table are practically insoluble in boiling trichloroethylene. The product of Example 3 is soluble at 20% by weight in methanol/H₂O (85:15), and the solutions are still stable after several months. The solubility of the copolyamides in

aqueous alcohols decreases inversely with the proportion of polylauro lactam. The same results are obtained if the amounts of ϵ -aminocaproic acid given in the Table are replaced by an equivalent amount of ϵ -caprolactam.

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WHAT WE CLAIM IS:—

1. A process for the preparation of copolyamides having a random distribution of the monomer units throughout the molecule in which ϵ -caprolactam or ϵ -aminocaproic acid or both are heated with hexamethylene diamine adipate and polylauro lactam in an inert atmosphere at atmospheric pressure to 260—290°C with consequent breakdown of the polylauro lactam to lauro lactam monomer units and the mixture held at this temperature until the random distribution is achieved.

2. A process according to claim 1 in which the polymerisation is continued for at least 8 hours at 290°C.

3. A process according to claim 1 in which the polymerisation is continued for at least 12 hours at 260°C.

4. A process according to any one of the preceding claims in which the mixture to be copolymerised is composed of 10 to 60% by weight of ϵ -caprolactam or ϵ -aminocaproic acid or both, 10 to 50% by weight of hexamethylene diamine adipate and 5 to 70% by weight of polylauro lactam.

5. A process according to any one of the preceding claims in which the polylauro lactam has a relative viscosity of 1.4 to 1.7 (measured in a 0.5% solution in *m*-cresol at 20°C).

6. A process according to any one of the preceding claims in which the mixture to be copolymerised also contains 1.2 to 1.5 mol % of an organic carboxylic acid chain growth regulator.

7. A process according to claim 6 in which the acid is sebacic acid.

8. A process according to claim 1 substantially as described with reference to any one of Examples 1 to 22 in the Table herein.

9. A copolyamide prepared by a process according to any one of the preceding claims.

10. A 6/66/12 copolyamide having a random distribution of monomer units in the molecule and containing 10 to 60% by weight of monomer units derived from ϵ -caprolactam or ϵ -aminocaproic or both, 10 to 50% by weight of monomer units derived from hexamethylene diamine adipate and 5 to 70% by weight of monomer units derived from lauro lactam.

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